Color Characteristics of Copper Phthalocyanine and its Chlorinated Derivatives

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Copper phthalocyanine pigments range in shade from blue to green, and are very strong and bright. Arranged in order of increasing greenness or of decreasing redness, they are listed as follows:

(1) Copper phthalocyanine (β-form)
(2) Copper phthalocyanine (α-form)
(3) Copper semichlorophthalocyanine
(4) Copper polychlorophthalocyanine

They are used as coloring matters dispersed in various vehicles such as polymerized linseed oil, nitrocellulose and miscellaneous synthetic resins.

In order to study the effects of the crystal structures, the numbers and positions of chlorine atoms and the pigment contents on the variation of color, the author formulated coloring matter with polymerized linseed oil used as the vehicle, and measured the reflectance curves.

Experimental

Materials.—*α-Form* (I) *and β-form* (II) *copper phthalocyanines.* — A mixture of phthalic anhydride, urea and cuprous chloride was heated in trichlorobenzene at about 190°C for 3 hr[1]. The reaction product was treated with 5% hydrochloric acid and 2% caustic soda, filtered off, washed with water and ethanol, and dried.

The crystal structure of copper phthalocyanine thus prepared was α-form (I)[2,3]. It was pulverized in a ball mill by the method described in Ref. 4.

To transform it into β-form (II), it was dissolved in 98% sulfuric acid, poured into water and deposited as fine crystals[5].

Copper octa-(4,5)-chlorophthalocyanine (III) *and copper octa-(3,6)-chlorophthalocyanine* (IV).— First, from the mixture of dichlorophthalic anhydrides prepared by chlorinating phthalic anhydride in oleum by the improved V. Villiger's method[6,7], 4,5-dichlorophthalic anhydride, m. p. 185.5~186.5°C (reported m. p. 185~187°C[8]) (*Anal.* Found: Cl, 32.66%) and 3,6-dichlorophthalic anhydride, m. p. 190~191°C (reported m. p. 190~191°C[8]) (*Anal.* Found: Cl, 32.71%) were separated with toluene-ethanol (1:1) solvent.

III (*Anal.* Found: Cl, 33.21%) and IV (*Anal.* Found: Cl, 33.23%) were synthesized respectively from 4,5- and 3,6-dichlorophthalic anhydrides by the urea-method[1]. They were respectively dissolved in chlorosulfonic acid and poured into ice water and reprecipitated as fine crystals.

Copper hexadecachlorophthalocyanine (V). — V was prepared by chlorinating copper octa-(3,6)-chlorophthalocyanine (*Anal.* Found: Cl, 50.33%)[7]. It was dissolved in chlorosulfonic acid, poured into ice water and reprecipitated as fine crystals. Particle size distributions of these materials were obtained with an electron microscope[9]. The diameters of these particles were 200~400 mμ and the mean value was about 250 mμ.

Methods.—A mixture of an equal quantity of each pigment and polymerized linseed oil was made into paste (A) by grinding 400 rounds in a Hoover automatic muller. A mixture of an equal quantity of aluminum hydroxide and polymerized linseed oil was made into paste (B) as above. A and B were mixed and pastes of each pigment, having pigment contents of 30, 25, 20, 15, 10, 7.5 and 5%, respectively, were prepared. These were applied 0.5 mm. in thickness on coated papers with a bladeoapplicator (Gardner Laboratory) and dried at room temperature. Reflectance curves of these samples were measured with a recording spectrophotometer (General Electric Co.) and C. I. E. Notations were obtained.

Results

Tables I, II, III, IV and V show the C. I. E. Notations of I, II, III, IV and V. In these tables, *Y* denotes luminosity, *Pe* purity and λ_D dominant wavelength.

TABLE I. C. I. E. NOTATIONS OF COPPER PHTHALOCYANINE (α-form)

Pig. cont. %	*Y* %	*Pe* %	λ_D mμ
30	8.42	50.2	465.5
25	9.10	51.0	466.0
20	10.62	51.8	470.2
15	12.40	51.0	471.9
10	16.60	49.1	475.4
7.5	18.28	47.1	476.4
5	25.08	40.2	478.2

TABLE II. C. I. E. NOTATIONS OF COPPER PHTHALOCYANINE (β-form)

Pig. cont. %	*Y* %	*Pe* %	λ_D mμ
30	7.64	50.0	463.0
25	8.52	52.5	464.1
20	9.44	52.0	466.2
15	10.37	51.2	469.4
10	15.10	47.5	472.4
7.5	17.49	44.8	474.8
5	23.18	38.4	476.2

TABLE III. C. I. E. NOTATIONS OF COPPER OCTA-(4,5)-CHLOROPHTHALOCYANINE

Pig. cont. %	*Y* %	*Pe* %	λ_D mμ
30	9.86	49.7	466.4
25	10.85	49.8	468.5
20	12.59	49.2	470.6
15	14.29	47.0	474.4
10	18.29	43.5	478.5
7.5	20.43	40.6	480.8
5	27.15	33.4	482.4

TABLE IV. C. I. E. NOTATIONS OF COPPER OCTA-(3,6)-CHLOROPHTHALOCYANINE

Pig. cont. %	*Y* %	*Pe* %	λ_D mμ
30	10.45	49.2	474.0
25	11.05	48.0	474.4
20	13.17	46.0	476.2
15	15.00	43.1	479.1
10	19.25	38.4	482.1
7.5	23.62	33.5	484.0
5	30.24	31.5	486.1

1) U. S. Pat. 2,197,458 (1940).
2) J. M. Robertson, *J. Chem. Soc.*, **1935**, 615; ibid., **1936**, 1195; ibid., **1937**, 219.
3) M. Shigemitsu, This Bulletin, **32**, 607 (1959).
4) U. S. Pat. 2,556,726 (1951); U. S. Pat. 2,556,727 (1951); U. S. Pat. 2556,728 (1951); U. S. Pat. 2,556,730 (1951).
5) G. von Susich, *Anal. Chem.*, **22**, 425 (1950).
6) V. Villiger, *Ber.*, **42**, 3538 (1909).
7) M. Shigemitsu, to be published in *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 112 (1959), (presented at the Autumnal Joint Meeting of Chemical Society of Japan with other Societies, Tokyo, 1957).
8) V. Villiger, *Ber.*, **42**, 3532 (1957).
9) E. Suito et al., presented at the 58th Meeting of Electron Microscope Committee of Japan, 1951.

TABLE V. C. I. E. NOTATIONS OF COPPER HEXADECACHLOROPHTHALOCYANINE

Pig. cont. %	*Y* %	*Pe* %	λ_D mμ
30	10.14	49.4	479.0
25	10.45	46.3	479.2
20	12.50	42.9	480.5
15	15.06	39.1	483.0
10	20.84	34.4	486.8
7.5	25.56	30.5	489.3
5	34.24	28.5	492.0

In all cases, luminosities and dominant wavelengths decreased as the pigment contents increased, but variations of purities differed depending upon the kinds of pigments. I and II gave the maximum purities when their pigment contents were 20 and 25% respectively. On the other hand, purities of IV and V increased as their pigment contents increased. III showed a tendency similar to I and II. Fig. 1 shows the relation between purities and luminosities.

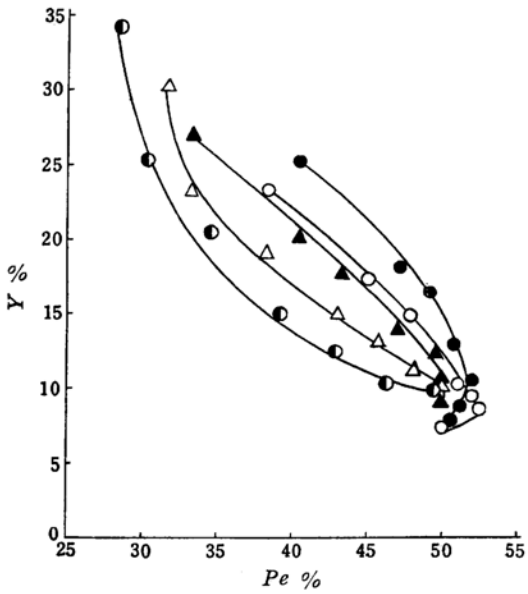

Fig. 1 Relation between purity and luminosity.
-●- Copper phthalocyanine (β-form).
-○- Copper phthalocyanine (α-form).
-▲- Copper octa-(4, 5)-chlorophthalocyanine.
-△- Copper octa-(3, 6)-chlorophthalocyanine.
-◐- Copper hexadecachlorophthalocyanine.

The purity of II was higher than that of I. The luminosities of I and II increased and decreased from the points of maximum purities with the variations in their purities, and the tendency in II was more conspicuous than in I. On the other hand, the luminosities of IV and V decreased with the increase in their purities.

Summary

The variation of color of copper phthalocyanine and its chlorinated derivatives in polymerized linseed oil was investigated.

The β-form of copper phthalocyanine is more conspicuous than the α-form in their variation of color.

Chlorine atoms at 3, 6- or 4, 5-positions of phthalocyanine nucleus give very different actions according to their variations of color, even if their chlorine contents are the same.

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